PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-235130
(43)Date of publication of application : 23.08.2002

(51)Int.CI.
C22C 5/06
C23C 14/06
C23C 14/14
C23C 14/34
G11B 7/24
G11B 7/26

(21)Application number : 2001-027864
(22)Date of filing : 05.02.2001

(71)Applicant : SUMITOMO METAL MINING CO LTD
(72)Inventor : SHIMIZU JUICHI
NAKAI TSUKASA

(54) SILVER ALLOY FOR OPTICAL DISK REFLECTION FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To produce a silver alloy which has high reflectivity and high thermal conductivity, simultaneously exhibits good corrosion resistance, and is used as a reflection film for an optical disk corresponding to high recording density.
SOLUTION: A silver alloy having a composition (1) containing 1 to 20 mass% Zn, and the balance Ag with inevitable impurities, or a composition (2) containing 1 to 20 mass% Zn and one or more kinds selected from Pd and Au by 0.1 to 15 mass%, and the balance Ag with inevitable impurities is used as a target to deposit an optical disk reflection film.

LEGAL STATUS
[Date of request for examination]
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number]
[Date of registration]
[Number of appeal against examiner's decision

of rejection]
[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

CLAIMS

[Claim(s)]
[Claim 1] The silver alloy for optical disk reflective film characterized by the remainder consisting of Ag and an unescapable impurity 1-20 mass % Including Zn.
[Claim 2] The silver alloy for optical disk reflective film characterized by the remainder consisting of Ag and an unescapable impurity 0.1-15 mass % More than including a kind of Pd and Au 1-20 mass % Including Zn.
[Claim 3] The sputtering target which consists of a silver alloy according to claim 1 or 2.
[Claim 4] Optical disk reflective film which consists of a silver alloy according to claim 1 or 2.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the silver alloy used as reflective film of various optical recording disks.
[0002]
[Description of the Prior Art] Various optical recording disks (the following, optical disk), such as CD, CD-R, CD-RW, DVD, DVD-RW, DVD+RW, DVD-RAM, and MOD, MD, are used as a medium which records computer information, image information, or music information.
[0003] Although the structure of these optical disks changes with play back systems, respectively, typically, it is common in that it has laminating cross-section structure forming the thin film which has various functions in the shape of a layer on the transparent substrate made from plastics, and by forming a lower protective layer, a record layer, an up protective layer, a reflective heat dissipation layer, and an overcoat layer. This reflective heat dissipation layer is the reflective film set as the object of this invention.
[0004] The reflective film has the function to reflect the laser light used for R/W of record, and aluminum, Au, Ag, and the thin film that consists of those alloys are mainly used.
[0005] Properties, such as that a reflection factor is high, a thermally conductive high thing, and a corrosion resistance high thing, are required of the reflective film. Especially, corresponding to a raise in the recording density of an optical disk, the demand of the reflective film equipped with both a high reflection factor and high thermal conductivity has been increasing.
[0006] While carrying out a deer It has the trouble that a reflection factor and thermal conductivity are low about both aluminum. A price being very high about Au and applying to a mass-production article has the trouble of being difficult. Further about Ag Although a reflection factor and thermal conductivity are high, it has the trouble that the corrosion resistance over oxidization or sulfuration is low, and the trouble of property degradation of the disk by rewriting, and the reflective film with which are completely satisfied of demand characteristics is not obtained.

[0007]
[Problem(s) to be Solved by the Invention] While the purpose of this invention has a high reflection factor and high thermal conductivity in view of this point, it shows good corrosion resistance and is to offer the silver alloy used as reflective film for the optical disk corresponding to high recording density.
[0008]
[Means for Solving the Problem] In order to attain the above-mentioned purpose, 1-20 mass % Including (1) Zn, the remainder consists of Ag and an unescapable impurity, or, as for the silver alloy for optical disk reflective film of this invention, the remainder consists of Ag and an unescapable impurity 0.1-15 mass % More than including a kind of Pd and Au 1-20 mass % Including (2) Zn.
[0009] As for the optical disk reflective film of this invention, it is desirable to form using said silver alloy as a target.
[0010]
[Embodiment of the Invention] Below, the detail of the component of this invention is explained.
[0011] this invention persons found out that it was possible to maintain many properties in the suitable range by adding Zn to Ag, as a result of performing various examination.
[0012] (1) Form the optical disk reflective film 1-20 mass % Including Zn, using as a target the silver alloy with which the remainder consists of Ag and an unescapable impurity, or the remainder consists of Ag and an unescapable impurity 0.1-15 mass % More than including a kind of Pd and Au 1-20 mass % Including (2) Zn.
[0013] The addition of concentration of Zn is too low at under 1 mass %, and since there is little effectiveness of corrosion-resistant improvement, property degradation of the optical disk by rewriting occurs. It it exceeds 20 mass %, the reflection factor of a silver alloy and thermal conductivity fall, and correspondence becomes impossible to a raise in the recording density of an optical disk.
[0014] Furthermore, more than in a kind of Pd and Au, although you may also contain, it 0.1-15 mass % Is the element which has the effectiveness that Pd and Au raise corrosion resistance further, and in the case of the optical disk using the protective coat containing ZnS, it is especially effective to make these elements contain.
[0015] The addition of concentration more than a kind of Pd and Au is too low at under 0.1 mass %, and there is little effectiveness of corrosion-resistant improvement. When 15 mass % is exceeded, the thermal conductivity of a silver alloy falls and it becomes impossible to correspond to high recording density-ization of an optical disk.
[0016] There is the following approach in formation of a reflective heat dissipation layer.
[0017] (1) How to choose quantity and a location, arrange the chip of the alloying element of 5x5x0.5 [mm], and carry out a spatter on a pure Ag target, according to the target concentration, (on chip law).
[0018] (2) How to carry out a spatter to a pure Ag target using the target (multicomponent target) which embedded the pellet of the target alloy element.
[0019] (3) How to carry out a spatter using the target (for it to be called a mixed sintered compact target on these specifications) which mixed Ag powder and the metal powder used as an alloy, and was produced in hot pressing etc.
[0020] (4) How to carry out a spatter using the alloy target produced with the solution process. A solution process is an approach the element to add performs the atmospheric-air dissolution, vacuum melting, and the argon gas ambient atmosphere dissolution.

[0021] A substrate is made to rotate or a substrate is made to rotate and revolve around the sun by the approach using the multicomponent target of the method of (1) on chip, and (2). A substrate is made to stand it still in (3) of others, and (4).
[0022] Moreover, by the approach using the multicomponent target of the method of (1) on chip, and (2), the thing of the purity of 99.99 mass % (4Ns) is used, respectively as the chip of a pure Ag target and an alloying element, and a pellet of an alloy element. By the approach of (3), Ag powder and the metal powder used as an alloy also use the thing of the purity of 99.99 mass % (4Ns), respectively. By the approach of (4), the shot of Ag metal which is a raw material, and an alloying element, or raw material powder also uses the thing of the purity of 99.99 mass % (4Ns), respectively.
[0023] In addition, when the range of the presentation of the sputtering target for forming the reflective film is specified, although the presentations of the reflective film formed using this sputtering target differ the range and a little [said], both are included in this invention. That is, also in the state of substrate quiescence, most of a target presentation and a film presentation does not have a presentation gap, and the silver alloy which was used for formation of a reflective heat dissipation layer according to the experiment of this invention persons found [of the presentation within a substrate / homogeneous] that they were good, when using the alloy target produced with the solution process, and the mixed sintered compact target. Moreover, when using these alloy targets and a mixed sintered compact target, it was high, and the membrane formation rate was also stable and suitable as a sputtering target.
[0024] The measuring method concerning many properties of the silver alloy for reflective film of the optical disk of this invention is explained below.
[0025] Measurement of the thermal conductivity of a thermal conductivity reflective heat dissipation layer is very difficult when thickness is thin. In a conventional patent official report, various kinds of conventional papers, etc., evaluation of presuming membranous thermal conductivity using a Wiedemann-Franz rule from the measured value of electrical resistivity is performed. However, although he needs to examine the sample to measure enough in order to use this approach, the case where it cannot necessarily be said that it is enough can see. Therefore, this invention persons evaluated by two approaches shown below, and examined the validity enough.
[0026] The 1st approach is an approach of measuring membranous electrical resistivity (conductivity) by the direct-current 4 terminal method, and asking for thermal conductivity by (1) type according to a Wiedemann-Franz rule.
[0027]
Lambda-rho/T=L 0= 2.43x10-8 [W-omega/K 2] ..... (1)
[0028] Here, for lambda, membranous thermal conductivity [W/m-K] and rho of electrical resistivity [omega-cm] and T are [temperature (absolutely) [K] and L0] Lorentz numbers [W-omega/K 2]. in addition, measurement of electrical resistivity rho -- four probes and Van der Pauw -- law may be used.
[0029] The 2nd approach is an approach of measuring [a membranous thermal diffusivity] a membranous consistency for the membranous specific heat further by DSC (differential scanning calorimeter) with AC calorimetric method, respectively, and asking for membranous thermal conductivity by (2) types.
[0030] Lambda=alpha-Cp-rhod ..... (2)
[0031] Here, for lambda, membranous thermal conductivity [W/m-K] and alpha are [the specific heat [J/g-K] and rhod of a thermal diffusivity [cm2/sec] and Cp] consistencies [g/cm3]. All

measurement was made into the inside of a room temperature (25 [**]) and a vacuum.
[0032] The 1st method of calculating thermal conductivity lambda using a Wiedemann-Franz rule from the measured value of electrical resistivity (conductivity) rho is very simple as compared with the 2nd method of calculating thermal conductivity lambda from the measured value of the thermal diffusivity alpha by AC calorimetric method, the measured value of the specific heat Cp by DSC, and the measured value of membranous consistency rhod.
[0033] The reflection factor of a reflection factor reflective heat dissipation layer carried out having covered [which was formed on the glass substrate] it over the spectrophotometer.
[0034] this invention persons examined sulfuration degradation of a reflective heat dissipation layer, and measured by the following approaches.
[0035] (1) First, form the thin film of a silver alloy on a glass substrate. Thickness was set to 3000 [**].
[0036] (2) The isolation S of number mass % (sulfur) exists in the ZnS powder which is the raw material powder of ZnS+SiO2 target. This was analyzed, only fixed time amount (for example, 24 [h]) fed the thin film of the silver alloy which formed membranes to the glass substrate into the ZnS powder which made isolation S (sulfur) 1 mass %, and change of the reflection factor before and behind an injection was measured.
[0037] From the reflection factor of the sample before an injection, the rate of change of a reflection factor deducted the reflection factor of the sample after an injection, broke it by the reflection factor of the sample before an injection, took the absolute value, hung 100, and made the unit [%].
[0038] Measurement of a disk property disk property was examined by the following approaches.
[0039] In the optical disk of CD system, it let the lens of NA0.55 pass, the semiconductor laser light of wavelength 780 [nm] was narrowed down to the diameter of a spot of a diameter 1 [mum] in respect of the medium, and it carried out by irradiating from a substrate side.
[0040] In the optical disk of a DVD system, it let the lens of NA0.6 pass, the semiconductor laser light of wavelength 633 [nm] was narrowed down to the diameter of a spot of a diameter 0.5 [mum] in respect of the medium, and it carried out by irradiating from a substrate side.
[0041] The laser power Pw at the time of record was changed to 8-16 [mW], having used laser power as Pe/Pw=0.5 with each linear velocity by fully crystallizing the whole disk surface and making it into an initial (un-recording) condition, CNR (carrier pair noise ratio) was large, and CNR, jitter, and modulation factor (before a trial) at that time were measured by choosing the conditions to which a jitter becomes small. Here, Pe is the laser power at the time of elimination.
[0042] Then, CNR, the jitter, and the modulation factor (after a trial) were similarly measured for each optical disk with each linear velocity after 500-hour neglect in 80 degrees C and the condition of the high-humidity/temperature of 85%RH. An exam is called a high-humidity/temperature storage trial.
[0043] (Example) Although an example explains the concrete configuration of this invention in more detail below, this invention is not limited to these examples.
[0044] (10- examples 1, 2, 4, and 6, 12, 15, the examples 1 and 4 of a comparison) The optical disk of CD system was produced as follows.
[0045] A pitch 1.6 [mum], the thickness 1.2 to which the slot of the depth 50 [nm] was attached [mm], The polycarbonate substrate of a diameter 120 [mm] is produced with injection molding. By the spatter of the conditions moreover shown in Table 2, a lower protective layer, a record layer, Carry out sequential formation of the up protective layer, and the reflective heat

dissipation layer using the sputtering target of the target presentation shown in Table 1 is formed. Moreover, ultraviolet-rays hardening resin (UV hardening resin) was applied with the spin coat method, ultraviolet rays are irradiated, and were stiffened, 5 [mum] laminatings were carried out as an overcoat layer, and the optical disk of each CD system was produced.
[0046] 80 (SiO2) 20 film formed and obtained on conditions which are set to Zn:S=1:1 (ZnS) was used for the lower protective layer and the up protective layer. Therefore, the sputtering target which produced the sintered compact target of 80 (ZnS) (SiO2) 20 by hot pressing was used.
[0047] Moreover, the record layer was used as Ag5In6Sb60Te29 film. Therefore, the sputtering target which produced the alloy target of Ag5In6Sb60Te29 by hot pressing was used.
[0048] Although the reflective heat dissipation layer was the silver alloy film, it is the target presentation shown in Table 1, and was produced with the solution process among the four aforementioned approaches.
[0049] In membrane formation of each class, PURISUPATTA was performed more than at least 1.5 [kWh], and the ultimate vacuum in the chamber before spatter initiation carried out to below 6.0x10-5 [Pa].
[0050] (Examples 3, 5, 7-9, 13 and 14, examples 2 and 3 of a comparison) The optical disk of a DVD system was produced as follows.
[0051] A pitch 0.8 [mum], the thickness 0.6 to which the slot of the depth 30 [nm] was attached [mm], The polycarbonate substrate of a diameter 120 [mm] is produced with injection molding. By the spatter of the conditions moreover shown in Table 2, a lower protective layer, a record layer, Carry out sequential formation of the up protective layer, and the reflective heat dissipation layer using the sputtering target of the target presentation shown in Table 1 is formed. Moreover, ultraviolet-rays hardening resin (UV hardening resin) is applied with a spin coat method. Irradiate ultraviolet rays, stiffen them and 4 [mum] laminatings are carried out as an overcoat layer. Furthermore, the polycarbonate substrate (the so-called blank disc) of thickness 0.6 [mm] and a diameter 120 [mm] which is not formed at all was stuck using ultraviolet-rays hardening resin, and the optical disk of each DVD system was produced.
[0052] A presentation and the formation approach of a lower protective layer, a record layer, an up protective layer, and a reflective heat dissipation layer were performed like the above-mentioned.
[0053] In examples 1-15 and the examples 1-4 of a comparison, the presentation of a reflective heat dissipation layer and the thickness of each class were measured. A result is shown in Table 1 and 3.
[0054] The presentation of a reflective heat dissipation layer produced each film on the glass substrate, and analyzed by EPMA (Electron Probe Micro Analysis).
[0055]
[Table 1]

[0056]
[Table 2]

[0057]
[Table 3]

[0058] As the target presentation of Table 1 and the presentation of a reflective heat dissipation layer showed, change of Zn content was less than several %.
[0059] About examples 1-15 and the examples 1-4 of a comparison, the heat conductivity of a reflective heat dissipation layer, the reflection factor of a reflective heat dissipation layer, the rate of change of this reflection factor, and a disk property were measured. A result is shown in Table 4 and 5.
[0060] The sample for measurement of the electrical resistivity rho in said 1st approach formed membranes to the cover glass of 20x70x0.8 [mm], and was started and measured to 3x6 [mm]. Thickness is 3000 [**].
[0061] The sample for measurement of the thermal diffusivity alpha in said 2nd approach formed membranes to the same cover glass, and was started and measured to 10x4 [mm]. Thickness is 3000 [**].
[0062] Only need mass stripped off the sample which formed membranes to the same cover glass, and measurement of the specific heat Cp by DSC was set to the specimen container, and was carried out.
[0063] In addition, in advance of production of each sample for measurement, each presentation sample was produced beforehand, the X diffraction was performed about them, and the crystallinity was checked. Furthermore, that by which the defect in the film was produced on very few conditions was used for the sample for measurement of the above-mentioned electrical resistivity rho and a thermal diffusivity alpha.
[0064] Thus, since he fully examined the Measuring condition, the estimate of the thermal conductivity lambda calculated from the estimate of the thermal conductivity lambda calculated using the Wiedemann-Franz rule from the measured value of conductivity rho, the measured value of the thermal diffusivity alpha by AC calorimetric method and the measured value of the specific heat Cp by DSC, and the measured value of membranous consistency rhod was in agreement within the accuracy of measurement.
[0065] The reflection factor of a reflective heat dissipation layer measured with the spectrophotometer the film formed on the glass substrate in the range of wavelength 400-900 [nm]. Thickness is all 3000 [**] like measurement of electrical resistivity rho and a thermal diffusivity alpha.
[0066]
[Table 4]

[0067] In the sulfuration deterioration test, the making time of each Ag content film to the ZnS powder containing 1% of free sulfur was made into 24 hours, and thickness of Ag alloy which made membranes form on a glass substrate was set to 3000 [**].
[0068] The rate of change in injection order is shown in Table 4.
[0069] Moreover, while performing the sulfuration deterioration test, it doubled and the surface state was observed with the metaloscope.
[0070] Evaluations of a disk property are the optical disk of CD system, and the optical disk of a DVD system, and were performed on condition that each above.
[0071] Although the record layer after membrane formation was amorphous, on the occasion of measurement of a disk property, the whole disk surface was fully first crystallized with DC light

of 10 [mW] in respect of the medium.

[0072] Linear velocity of the optical disk at this time was made into 7.0 and two levels of 15.0 [m/sec] to the optical disk of CD system to the optical disk of three levels of 2.0, 5.0, and 10.0 [m/sec], and a DVD system. Reading power Pr was set to 0.9 [mW].

[0073] Then, the high-humidity/temperature storage trial was performed and CNR trial before and after a trial, the jitter, and the modulation factor were measured. A result is shown in Table 5.

[0074] About the example of this invention, the data of the worst linear velocity in each linear velocity are chosen as Table 5 as a representative, and are shown in it. Although it was almost the same also in which linear velocity about the example of a comparison, the data of the best linear velocity in each linear velocity are chosen as a representative, and are shown.

[0075]

[Table 5]

[0076] (Evaluation)

If the amount of an alloying element is made to increase, although thermal conductivity lambda falls, generally the variation changes also with elements to add, so that the thermal conductivity lambda of the thermal conductivity table 4 may also show.

[0077] Since the thermal conductivity lambda of the reflective heat dissipation layer demanded changes with film configurations (a presentation, thickness, etc.) in an optical disk, like examples 1-15, that it can carry out adjustable [of the thermal conductivity lambda] broadly with an alloying element in the range of this invention shows that the silver alloy of this invention can use it broadly, and it is very desirable.

[0078] Like the examples 2-4 of a comparison, if the amount of an alloying element is made to increase across the range of this invention, adjustable [of the thermal conductivity lambda] can be carried out further, but thermal conductivity lambda is too low, and since heat dissipation capacity becomes small, and the reflection factor described below is also reduced and it stops playing a reflective role, it is not desirable.

[0079] The silver alloy of this invention has a high reflection factor in the large wavelength range so that the reflection factor of the reflection factor table 4 may show. Moreover, since it can carry out adjustable [of the heat conductivity lambda] widely as mentioned above, it is the optimal as optical disk reflective heat dissipation film.

[0080] The silver alloy of this invention can suppress reactivity with S (sulfur) low so that the rate of change of the reflection factor of Table 4 may show. Therefore, the corrosion resistance over S (sulfur) was able to be raised.

[0081] When there is too little Zn to add like the example 1 of a comparison, the rate of change of a reflection factor is too large, and corrosion resistance becomes low practical less.

[0082] Like the examples 2-4 of a comparison, if this range is reached, as stated previously, thermal conductivity is too low, and since a reflection factor falls, it stops playing a role of a reflective heat dissipation layer, and is not desirable [if the amount of an alloying element is made to increase across the range of this invention, corrosion resistance can be raised further, but].

[0083] Although the cause that a reflection factor falls with a metaloscope etc. according to the result of having observed the surface state is in the phase of Ag_2S made to the surface of a silver alloy and is extent dotted with the point that it is black when contact time with S (sulfur) is short

comparatively, if this comes to exceed fixed time amount, even the whole film surface will be reached. In this process, a reflection factor decreases gradually. Although the cause by which this reaction occurs is because it is easy to combine silver and S (sulfur), it can control this sharply in the silver alloy of this invention.

[0084] As shown in the disk property table 5, when using the silver alloy of this invention for the reflective heat dissipation layer, the optical disk which has a good initial property could be produced, and change was hardly seen for CNR, a jitter, and a modulation factor after the high-humidity/temperature storage trial.

[0085] This shows that the corrosion resistance over the corrosion by moisture, i.e., oxidation, is also high while showing that corrosion resistance [as opposed to sulfuration in the silver alloy of this invention] is high. Therefore, the protective coat of various nitrides, such as for example, a SiN system without worries about the corrosion by sulfuration, an AlN system, and a ZrN system, Also when the protective coat of various oxides, such as 2OTa5 system, 2Oaluminum3 system, ZrO2 system, and a MgO system, and the protective coat of the carbide of a SiC system are used, by the case where ZnS+SiO2 system or a ZnS system is used for a protective coat Also when using a barrier layer or a diffusion prevention layer between an up protective coat and a reflective heat dissipation layer, it is considered to be useful to use the reflective heat dissipation layer of this invention when raising the dependability of a disk.

[0086] On the other hand, as for the optical disk of the example 1 of a comparison, CNR, the jitter, and the modulation factor were changing a lot after the high-humidity/temperature storage trial. The optical disk of the examples 2-4 of a comparison was difficult to have a good disk property in an initial property.

[0087] Analysis of various optical disks after a high-humidity/temperature storage trial checked that sulfuration of the silver alloy a reflective heat dissipation layer brings [silver alloy] a result like the example 1 of a comparison had influenced. As for bringing a result like the examples 2-4 of a comparison, it is mainly considered to be the causes that thermal conductivity is small about the silver alloy of a reflective heat dissipation layer and that a reflection factor is low.

[0088] The silver alloy of this invention has a high reflection factor, and its corrosion resistance over sulfuration is high so that he can understand easily from these results. Moreover, it has the description that the thermal conductivity of a reflective heat dissipation layer is a lot changeable, with the concentration of the element to add. The optical disk which maintains a good property between [from an initial property] after a high-humidity/temperature storage trial by this is producible.

[0089] It is thought that application also on the reflective film of the reflecting mirror for which the corrosion resistance other than the example of this inventions, such as an optical disk and a magneto-optic disk, is required, and the application which needs a high reflection factor, for example, corrosion resistance, is needed, the reflective film of lighting fitting, the reflective film for indicators, and the reflective film for reflectors is possible for the silver alloy of this invention.

[0090] Moreover, although this invention showed the example which formed membranes by the sputtering method, the reflective film of this invention is producible with various membrane formation techniques, such as vacuum evaporation technique, the ion plating method, and various various CVD methods, galvanizing methods.

[0091]

[Effect of the Invention] As mentioned above, as explained to the detail, while the silver alloy of this invention has a high reflection factor and high thermal conductivity, it shows good corrosion

resistance.
[0092] Moreover, it is thought that the silver alloy of this invention is very useful also to the reflecting mirror of a liquid crystal display (LCD), a plasma display (PDP), EL (electroluminescence) display, etc. which becomes important [heat dissipation]. Of course, since it is shown that that thermal conductivity is high has high conductivity, various corrosion resistance is required and to be useful is considered by various required wiring materials with small electrical resistivity etc.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the silver alloy used as reflective film of various optical recording disks.

PRIOR ART

[Description of the Prior Art] Various optical recording disks (the following, optical disk), such as CD, CD-R, CD-RW, DVD, DVD-RW, DVD+RW, DVD-RAM, and MOD, MD, are used as a medium which records computer information, image information, or music information.
[0003] Although the structure of these optical disks changes with play back systems, respectively, typically, it is common in that it has laminating cross-section structure forming the thin film which has various functions in the shape of a layer on the transparent substrate made from plastics, and by forming a lower protective layer, a record layer, an up protective layer, a reflective heat dissipation layer, and an overcoat layer. This reflective heat dissipation layer is the reflective film set as the object of this invention.
[0004] The reflective film has the function to reflect the laser light used for R/W of record, and aluminum, Au, Ag, and the thin film that consists of those alloys are mainly used.
[0005] Properties, such as that a reflection factor is high, a thermally conductive high thing, and a corrosion resistance high thing, are required of the reflective film. Especially, corresponding to a raise in the recording density of an optical disk, the demand of the reflective film equipped with both a high reflection factor and high thermal conductivity has been increasing.
[0006] While carrying out a deer It has the trouble that a reflection factor and thermal conductivity are low about both aluminum. A price being very high about Au and applying to a mass-production article has the trouble of being difficult. Further about Ag Although a reflection factor and thermal conductivity are high, it has the trouble that the corrosion resistance over oxidization or sulfuration is low, and the trouble of property degradation of the disk by rewriting, and the reflective film with which are completely satisfied of demand characteristics is not obtained.

EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, as explained to the detail, while the silver alloy of this invention has a high reflection factor and high thermal conductivity, it shows good corrosion resistance.
[0092] Moreover, it is thought that the silver alloy of this invention is very useful also to the reflecting mirror of a liquid crystal display (LCD), a plasma display (PDP), EL (electroluminescence) display, etc. which becomes important [heat dissipation]. Of course,

since it is shown that that thermal conductivity is high has high conductivity, various corrosion resistance is required and to be useful is considered by various required wiring materials with small electrical resistivity etc.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] While the purpose of this invention has a high reflection factor and high thermal conductivity in view of this point, it shows good corrosion resistance and is to offer the silver alloy used as reflective film for the optical disk corresponding to high recording density.

MEANS

[Means for Solving the Problem] In order to attain the above-mentioned purpose, 1-20 mass % Including (1) Zn, the remainder consists of Ag and an unescapable impurity, or, as for the silver alloy for optical disk reflective film of this invention, the remainder consists of Ag and an unescapable impurity 0.1-15 mass % More than including a kind of Pd and Au 1-20 mass % Including (2) Zn.
[0009] As for the optical disk reflective film of this invention, it is desirable to form using said silver alloy as a target.
[0010]
[Embodiment of the Invention] Below, the detail of the component of this invention is explained.
[0011] this invention persons found out that it was possible to maintain many properties in the suitable range by adding Zn to Ag, as a result of performing various examination.
[0012] (1) Form the optical disk reflective film 1-20 mass % Including Zn, using as a target the silver alloy with which the remainder consists of Ag and an unescapable impurity, or the remainder consists of Ag and an unescapable impurity 0.1-15 mass % More than including a kind of Pd and Au 1-20 mass % Including (2) Zn.
[0013] The addition of concentration of Zn is too low at under 1 mass %, and since there is little effectiveness of corrosion-resistant improvement, property degradation of the optical disk by rewriting occurs. It it exceeds 20 mass %, the reflection factor of a silver alloy and thermal conductivity fall, and correspondence becomes impossible to a raise in the recording density of an optical disk.
[0014] Furthermore, more than in a kind of Pd and Au, although you may also contain, it 0.1-15 mass % Is the element which has the effectiveness that Pd and Au raise corrosion resistance further, and in the case of the optical disk using the protective coat containing ZnS, it is especially effective to make these elements contain.
[0015] The addition of concentration more than a kind of Pd and Au is too low at under 0.1 mass %, and there is little effectiveness of corrosion-resistant improvement. When 15 mass % is exceeded, the thermal conductivity of a silver alloy falls and it becomes impossible to correspond to high recording density-ization of an optical disk.
[0016] There is the following approach in formation of a reflective heat dissipation layer.
[0017] (1) How to choose quantity and a location, arrange the chip of the alloying element of 5x5x0.5 [mm], and carry out a spatter on a pure Ag target, according to the target concentration, (on chip law).
[0018] (2) How to carry out a spatter to a pure Ag target using the target (multicomponent target)

which embedded the pellet of the target alloy element.

[0019] (3) How to carry out a spatter using the target (for it to be called a mixed sintered compact target on these specifications) which mixed Ag powder and the metal powder used as an alloy, and was produced in hot pressing etc.

[0020] (4) How to carry out a spatter using the alloy target produced with the solution process. A solution process is an approach the element to add performs the atmospheric-air dissolution, vacuum melting, and the argon gas ambient atmosphere dissolution.

[0021] A substrate is made to rotate or a substrate is made to rotate and revolve around the sun by the approach using the multicomponent target of the method of (1) on chip, and (2). A substrate is made to stand it still in (3) of others, and (4).

[0022] Moreover, by the approach using the multicomponent target of the method of (1) on chip, and (2), the thing of the purity of 99.99 mass % (4Ns) is used, respectively as the chip of a pure Ag target and an alloying element, and a pellet of an alloy element. By the approach of (3), Ag powder and the metal powder used as an alloy also use the thing of the purity of 99.99 mass % (4Ns), respectively. By the approach of (4), the shot of Ag metal which is a raw material, and an alloying element, or raw material powder also uses the thing of the purity of 99.99 mass % (4Ns), respectively.

[0023] In addition, when the range of the presentation of the sputtering target for forming the reflective film is specified, although the presentations of the reflective film formed using this sputtering target differ the range and a little [said], both are included in this invention. That is, also in the state of substrate quiescence, most of a target presentation and a film presentation does not have a presentation gap, and the silver alloy which was used for formation of a reflective heat dissipation layer according to the experiment of this invention persons found [of the presentation within a substrate / homogeneous] that they were good, when using the alloy target produced with the solution process, and the mixed sintered compact target. Moreover, when using these alloy targets and a mixed sintered compact target, it was high, and the membrane formation rate was also stable and suitable as a sputtering target.

[0024] The measuring method concerning many properties of the silver alloy for reflective film of the optical disk of this invention is explained below.

[0025] Measurement of the thermal conductivity of a thermal conductivity reflective heat dissipation layer is very difficult when thickness is thin. In a conventional patent official report, various kinds of conventional papers, etc., evaluation of presuming membranous thermal conductivity using a Wiedemann-Franz rule from the measured value of electrical resistivity is performed. However, although he needs to examine the sample to measure enough in order to use this approach, the case where it cannot necessarily be said that it is enough can see. Therefore, this invention persons evaluated by two approaches shown below, and examined the validity enough.

[0026] The 1st approach is an approach of measuring membranous electrical resistivity (conductivity) by the direct-current 4 terminal method, and asking for thermal conductivity by (1) type according to a Wiedemann-Franz rule.

[0027]

Lambda-rho/T=L 0= 2.43x10-8 [W-omega/K 2] ..... (1)

[0028] Here, for lambda, membranous thermal conductivity [W/m-K] and rho of electrical resistivity [omega-cm] and T are [temperature (absolutely) [K] and L0] Lorentz numbers [W-omega/K 2]. in addition, measurement of electrical resistivity rho -- four probes and Van der Pauw -- law may be used.

[0029] The 2nd approach is an approach of measuring [a membranous thermal diffusivity] a membranous consistency for the membranous specific heat further by DSC (differential scanning calorimeter) with AC calorimetric method, respectively, and asking for membranous thermal conductivity by (2) types.
[0030] Lambda=alpha-Cp-rhod ..... (2)
[0031] Here, for lambda, membranous thermal conductivity [W/m-K] and alpha are [the specific heat [J/g-K] and rhod of a thermal diffusivity [cm2/sec] and Cp] consistencies [g/cm3]. All measurement was made into the inside of a room temperature (25 [**]) and a vacuum.
[0032] The 1st method of calculating thermal conductivity lambda using a Wiedemann-Franz rule from the measured value of electrical resistivity (conductivity) rho is very simple as compared with the 2nd method of calculating thermal conductivity lambda from the measured value of the thermal diffusivity alpha by AC calorimetric method, the measured value of the specific heat Cp by DSC, and the measured value of membranous consistency rhod.
[0033] The reflection factor of a reflection factor reflective heat dissipation layer carried out having covered [which was formed on the glass substrate] it over the spectrophotometer.
[0034] this invention persons examined sulfuration degradation of a reflective heat dissipation layer, and measured by the following approaches.
[0035] (1) First, form the thin film of a silver alloy on a glass substrate. Thickness was set to 3000 [**].
[0036] (2) The isolation S of number mass % (sulfur) exists in the ZnS powder which is the raw material powder of ZnS+SiO2 target. This was analyzed, only fixed time amount (for example, 24 [h]) fed the thin film of the silver alloy which formed membranes to the glass substrate into the ZnS powder which made isolation S (sulfur) 1 mass %, and change of the reflection factor before and behind an injection was measured.
[0037] From the reflection factor of the sample before an injection, the rate of change of a reflection factor deducted the reflection factor of the sample after an injection, broke it by the reflection factor of the sample before an injection, took the absolute value, hung 100, and made the unit [%].
[0038] Measurement of a disk property disk property was examined by the following approaches.
[0039] In the optical disk of CD system, it let the lens of NA0.55 pass, the semiconductor laser light of wavelength 780 [nm] was narrowed down to the diameter of a spot of a diameter 1 [mum] in respect of the medium, and it carried out by irradiating from a substrate side.
[0040] In the optical disk of a DVD system, it let the lens of NA0.6 pass, the semiconductor laser light of wavelength 633 [nm] was narrowed down to the diameter of a spot of a diameter 0.5 [mum] in respect of the medium, and it carried out by irradiating from a substrate side.
[0041] The laser power Pw at the time of record was changed to 8-16 [mW], having used laser power as Pe/Pw=0.5 with each linear velocity by fully crystallizing the whole disk surface and making it into an initial (un-recording) condition, CNR (carrier pair noise ratio) was large, and CNR, jitter, and modulation factor (before a trial) at that time were measured by choosing the conditions to which a jitter becomes small. Here, Pe is the laser power at the time of elimination.
[0042] Then, CNR, the jitter, and the modulation factor (after a trial) were similarly measured for each optical disk with each linear velocity after 500-hour neglect in 80 degrees C and the condition of the high-humidity/temperature of 85%RH. An exam is called a high-humidity/temperature storage trial.

EXAMPLE

(Example) Although an example explains the concrete configuration of this invention in more detail below, this invention is not limited to these examples.
[0044] (10- examples 1, 2, 4, and 6, 12, 15, the examples 1 and 4 of a comparison) The optical disk of CD system was produced as follows.
[0045] It is injection molding about the polycarbonate substrate of thickness 1.2 [mm] and a diameter 120 [mm] to which the slot of a pitch 1.6 [mum] and the depth 50 [nm] was attached. On it, by the spatter of the conditions which were produced and were shown in Table 2 A lower protective layer, Carry out sequential formation of a record layer and the up protective layer, and the reflective heat dissipation layer using the sputtering target of the target presentation shown in Table 1 is formed. Moreover, ultraviolet-rays hardening resin (UV hardening resin) was applied with the spin coat method, ultraviolet rays are irradiated, and were stiffened, 5 [mum] laminatings were carried out as an overcoat layer, and the optical disk of each CD system was produced.
[0046] 80 (SiO2) 20 film formed and obtained on conditions which are set to Zn:S=1:1 (ZnS) was used for the lower protective layer and the up protective layer. Therefore, the sputtering target which produced the sintered compact target of 80 (ZnS) (SiO2) 20 by hot pressing was used.
[0047] Moreover, the record layer was used as Ag5In6Sb60Te29 film. Therefore, the sputtering target which produced the alloy target of Ag5In6Sb60Te29 by hot pressing was used.
[0048] Although the reflective heat dissipation layer was the silver alloy film, it is the target presentation shown in Table 1, and was produced with the solution process among the four aforementioned approaches.
[0049] In membrane formation of each class, PURISUPATTA was performed more than at least 1.5 [kWh], and the ultimate vacuum in the chamber before spatter initiation carried out to below 6.0x10-5 [Pa].
[0050] (Examples 3, 5, 7-9, 13 and 14, examples 2 and 3 of a comparison) The optical disk of a DVD system was produced as follows.
[0051] It is injection molding about the polycarbonate substrate of thickness 0.6 [mm] and a diameter 120 [mm] to which the slot of a pitch 0.8 [mum] and the depth 30 [nm] was attached. On it, by the spatter of the conditions which were produced and were shown in Table 2 A lower protective layer, Carry out sequential formation of a record layer and the up protective layer, and the reflective heat dissipation layer using the sputtering target of the target presentation shown in Table 1 is formed. Moreover, ultraviolet-rays hardening resin (UV hardening resin) is applied with a spin coat method. Irradiate ultraviolet rays, stiffen them and 4 [mum] laminatings are carried out as an overcoat layer. Furthermore, the polycarbonate substrate (the so-called blank disc) of thickness 0.6 [mm] and a diameter 120 [mm] which is not formed at all was stuck using ultraviolet-rays hardening resin, and the optical disk of each DVD system was produced.
[0052] A presentation and the formation approach of a lower protective layer, a record layer, an up protective layer, and a reflective heat dissipation layer were performed like the above-mentioned.
[0053] In examples 1-15 and the examples 1-4 of a comparison, the presentation of a reflective heat dissipation layer and the thickness of each class were measured. A result is shown in Table 1 and 3.
[0054] The presentation of a reflective heat dissipation layer produced each film on the glass

substrate, and analyzed by EPMA (Electron Probe Micro Analysis).
[0055]
[Table 1]

[0056]
[Table 2]

[0057]
[Table 3]

[0058] As the target presentation of Table 1 and the presentation of a reflective heat dissipation layer showed, change of Zn content was less than several %.
[0059] About examples 1-15 and the examples 1-4 of a comparison, the heat conductivity of a reflective heat dissipation layer, the reflection factor of a reflective heat dissipation layer, the rate of change of this reflection factor, and a disk property were measured. A result is shown in Table 4 and 5.
[0060] The sample for measurement of the electrical resistivity rho in said 1st approach formed membranes to the cover glass of 20x70x0.8 [mm], and was started and measured to 3x6 [mm]. Thickness is 3000 [**].
[0061] The sample for measurement of the thermal diffusivity alpha in said 2nd approach formed membranes to the same cover glass, and was started and measured to 10x4 [mm]. Thickness is 3000 [**].
[0062] Only need mass stripped off the sample which formed membranes to the same cover glass, and measurement of the specific heat Cp by DSC was set to the specimen container, and was carried out.
[0063] In addition, in advance of production of each sample for measurement, each presentation sample was produced beforehand, the X diffraction was performed about them, and the crystallinity was checked. Furthermore, that by which the defect in the film was produced on very few conditions was used for the sample for measurement of the above-mentioned electrical resistivity rho and a thermal diffusivity alpha.
[0064] Thus, since he fully examined the Measuring condition, the estimate of the thermal conductivity lambda calculated from the estimate of the thermal conductivity lambda calculated using the Wiedemann-Franz rule from the measured value of conductivity rho, the measured value of the thermal diffusivity alpha by AC calorimetric method and the measured value of the specific heat Cp by DSC, and the measured value of membranous consistency rhod was in agreement within the accuracy of measurement.
[0065] The reflection factor of a reflective heat dissipation layer measured with the spectrophotometer the film formed on the glass substrate in the range of wavelength 400-900 [nm]. Thickness is all 3000 [**] like measurement of electrical resistivity rho and a thermal diffusivity alpha.
[0066]
[Table 4]

[0067] In the sulfuration deterioration test, the making time of each Ag content film to the ZnS powder containing 1% of free sulfur was made into 24 hours, and thickness of Ag alloy which made membranes form on a glass substrate was set to 3000 [**].
[0068] The rate of change in injection order is shown in Table 4.
[0069] Moreover, while performing the sulfuration deterioration test, it doubled and the surface state was observed with the metaloscope.
[0070] Evaluations of a disk property are the optical disk of CD system, and the optical disk of a DVD system, and were performed on condition that each above.
[0071] Although the record layer after membrane formation was amorphous, on the occasion of measurement of a disk property, the whole disk surface was fully first crystallized with DC light of 10 [mW] in respect of the medium.
[0072] Linear velocity of the optical disk at this time was made into 7.0 and two levels of 15.0 [m/sec] to the optical disk of CD system to the optical disk of three levels of 2.0, 5.0, and 10.0 [m/sec], and a DVD system. Reading power Pr was set to 0.9 [mW].
[0073] Then, the high-humidity/temperature storage trial was performed and CNR trial before and after a trial, the jitter, and the modulation factor were measured. A result is shown in Table 5.
[0074] About the example of this invention, the data of the worst linear velocity in each linear velocity are chosen as Table 5 as a representative, and are shown in it. Although it was almost the same also in which linear velocity about the example of a comparison, the data of the best linear velocity in each linear velocity are chosen as a representative, and are shown.
[0075]
[Table 5]

[0076] (Evaluation)
If the amount of an alloying element is made to increase, although thermal conductivity lambda falls, generally the variation changes also with elements to add, so that the thermal conductivity lambda of the thermal conductivity table 4 may also show.
[0077] Since the thermal conductivity lambda of the reflective heat dissipation layer demanded changes with film configurations (a presentation, thickness, etc.) in an optical disk, like examples 1-15, that it can carry out adjustable [of the thermal conductivity lambda] broadly with an alloying element in the range of this invention shows that the silver alloy of this invention can use it broadly, and it is very desirable.
[0078] Like the examples 2-4 of a comparison, if the amount of an alloying element is made to increase across the range of this invention, adjustable [of the thermal conductivity lambda] can be carried out further, but thermal conductivity lambda is too low, and since heat dissipation capacity becomes small, and the reflection factor described below is also reduced and it stops playing a reflective role, it is not desirable.
[0079] The silver alloy of this invention has a high reflection factor in the large wavelength range so that the reflection factor of the reflection factor table 4 may show. Moreover, since it can carry out adjustable [of the heat conductivity lambda] widely as mentioned above, it is the optimal as optical disk reflective heat dissipation film.
[0080] The silver alloy of this invention can suppress reactivity with S (sulfur) low so that the rate of change of the reflection factor of Table 4 may show. Therefore, the corrosion resistance

over S (sulfur) was able to be raised.

[0081] When there is too little Zn to add like the example 1 of a comparison, the rate of change of a reflection factor is too large, and corrosion resistance becomes low practical less.

[0082] Like the examples 2-4 of a comparison, if this range is reached, as stated previously, thermal conductivity is too low, and since a reflection factor falls, it stops playing a role of a reflective heat dissipation layer, and is not desirable [if the amount of an alloying element is made to increase across the range of this invention, corrosion resistance can be raised further, but].

[0083] Although the cause that a reflection factor falls with a metaloscope etc. according to the result of having observed the surface state is in the phase of Ag2S made to the surface of a silver alloy and is extent dotted with the point that it is black when contact time with S (sulfur) is short comparatively, if this comes to exceed fixed time amount, even the whole film surface will be reached. In this process, a reflection factor decreases gradually. Although the cause by which this reaction occurs is because it is easy to combine silver and S (sulfur), it can control this sharply in the silver alloy of this invention.

[0084] As shown in the disk property table 5, when using the silver alloy of this invention for the reflective heat dissipation layer, the optical disk which has a good initial property could be produced, and change was hardly seen for CNR, a jitter, and a modulation factor after the high-humidity/temperature storage trial.

[0085] This shows that the corrosion resistance over the corrosion by moisture, i.e., oxidation, is also high while showing that corrosion resistance [as opposed to sulfuration in the silver alloy of this invention] is high. Therefore, it is between an up protective coat and a reflective heat dissipation layer by the case where ZnS+SiO2 system or a ZnS system is used for a protective coat also when [that there are no worries about the corrosion by sulfuration] the protective coat of various oxides, such as a protective coat of various nitrides, such as a SiN system, an AlN system, and a ZrN system, 2OTa5 system, 2Oaluminum3 system, ZrO2 system, and a MgO system, and the protective coat of the carbide of a SiC system are used, for example. Also when using a barrier layer or a diffusion prevention layer, it is considered to be useful to use the reflective heat dissipation layer of this invention when raising the dependability of a disk.

[0086] On the other hand, as for the optical disk of the example 1 of a comparison, CNR, the jitter, and the modulation factor were changing a lot after the high-humidity/temperature storage trial. The optical disk of the examples 2-4 of a comparison was difficult to have a good disk property in an initial property.

[0087] Analysis of various optical disks after a high-humidity/temperature storage trial checked that sulfuration of the silver alloy a reflective heat dissipation layer brings [silver alloy] a result like the example 1 of a comparison had influenced. As for bringing a result like the examples 2-4 of a comparison, it is mainly considered to be the causes that thermal conductivity is small about the silver alloy of a reflective heat dissipation layer and that a reflection factor is low.

[0088] The silver alloy of this invention has a high reflection factor, and its corrosion resistance over sulfuration is high so that he can understand easily from these results. Moreover, it has the description that the thermal conductivity of a reflective heat dissipation layer is a lot changeable, with the concentration of the element to add. The optical disk which maintains a good property between [from an initial property] after a high-humidity/temperature storage trial by this is producible.

[0089] It is thought that application also on the reflective film of the reflecting mirror for which the corrosion resistance other than the example of this inventions, such as an optical disk and a

magneto-optic disk, is required, and the application which needs a high reflection factor, for example, corrosion resistance, is needed, the reflective film of lighting fitting, the reflective film for indicators, and the reflective film for reflectors is possible for the silver alloy of this invention.

[0090] Moreover, although this invention showed the example which formed membranes by the sputtering method, the reflective film of this invention is producible with various membrane formation techniques, such as vacuum evaporation technique, the ion plating method, and various various CVD methods, galvanizing methods.

G:\LIT\Academy\Target Tech\Prior Art vs. Nee\japan-235130.doc